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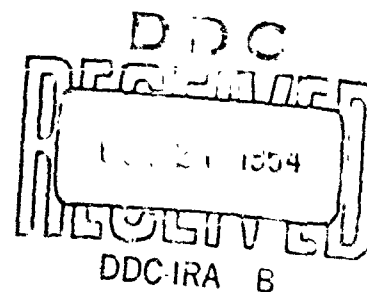
SEPARATION OF THE RARE EARTH ELEMENTS

Final Report

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Several procedures have been utilized for the separation of compounds of a mixture of rare earths into pure samples of compounds of the individual rare earths. These may be grouped into two general types: (1) fractional separations depending on slight differences in behavior of the individual elements and (2) unique reactions of one ion in a mixture of ions. In the first category are the following:

fractional crystallization,   fractional precipitation,

fractional decomposition,   varying rates of reaction,

fractional dissolution,   solvent extraction,

and use of ion exchange resins.

All procedures in the second category are dependent upon altering the oxidation state of one of the rare earth elements in a mixture whereby that element exhibits reactions different from the remaining elements.

It is interesting that, in the development of these procedures -- indeed, in the development of the basic chemistry of the rare earths -- comparatively little attention has been given to the coordination compounds of the rare earth elements. Nevertheless, the present knowledge of coordination compounds is such as to suggest that the application of well established principles probably would result in a distinct improvement in separation procedures in both categories.

The ways in which coordination compounds have been used in separations of metal ions are:

1. Formation of water insoluble compounds (occasionally nearly specific precipitants can be found such as dimethylglyoxime for nickel).

2. Formation of organic-solvent-soluble compounds (use of acetyl-acetone and TTA in solvent extraction separations).

3. Ion-sequestering (use of complexing agents such as citric acid and EDTA in ion-exchange separations).

From these considerations it would seem that a knowledge of the coordination behavior of the rare earths would be justified on the basis of the above possibilities alone. However there are other ways in which coordination compounds present attractive possibilities.

1. Possible variation of maximum coordination number across the rare earth series. The radii of the rare earth ions (M^{3+}) vary from 1.22 to 0.99 Å. It is conceivable that this variation in size is sufficient to cause a variation in the total number of atoms that can be packed around a rare earth ion. If so, it should be possible to design coordination agents which would separate ions above a certain size from those below this size.

2. Possible stabilization of oxidation states <3 and >3. Present methods of separating cerium from other rare earths are based on oxidizing the cerium to Ce^{4+}. Similarly, separations of europium, samarium and ytterbium are based on reduction to M^{2+}. It is conceivable that ligands can be found (1) which will stabilize states of oxidation <3 and >3 so as to make possible more satisfactory separations of Ce^{4+}, Sm^{2+}, Eu^{2+} and Yb^{2+} than those presently used and (2) which will so stabilize these same or other oxidation states as to make possible the separation of other rare earth elements.

3. Combinations of above effects with conventional methods of separation, especially, precipitations, solvent extraction, ion exchange, and chromatography.

A group of arsenic-containing amines was thought to offer promise in one or more of these approaches. However, despite the large number of organoarsenic compounds which have been prepared, there has been a surprising lack of systematic investigation of synthetic methods.

The following summary of a program of synthesis of some of these compounds describes work supported by this contract. Experimental details are given in a thesis by Robert F. Harris, submitted to the Graduate School of The Pennsylvania State University in June, 1963.

I. INTRODUCTICN

General Statement of the Problem

Some aminoalkylarsines were desired in connection with studies on the relative donor strength of various electronegative elements in coordination to rare earth metal ions The functional groups desired were the 3-aminopropyl- and the 2-aminoethyl- compounds in order that six and five membered rings respectively could be formed by coordination involving both the nitrogen and arsenic atoms. The successful preparation of an arsine of either type has never been reported.

A possible route for the preparation of 3-aminopropyl arsines is the reduction of the corresponding 2-cyanoethyl arsines Substituted 2-cyanoethyl arsines have been prepared by the condensation of the corresponding arsine with arcylonitrile. Tris(2-cyanoethyl)arsine has never been prepared.

A possible route for the preparation of 2-aminopropyl arsines is the condensation of the substituted arsine with ethyleneimine.

There is a definite lack of basic investigation into the preparation of substituted arsines by methods other than the amalgamated zinc reduction of arsenic acids or halides. There have been scattered reports of reduction of haloarsines with metal hydrides. Since substituted arsines are the starting point for nearly all of the compounds mentioned above, a more thorough investigation into their generation by hydride reduction appeared to be in order.

II. RESULTS AND DISCUSSION

A. Possible Existence of Substituted 3-Aminopropyl Arsines

The work of Cookson and Mann has been successfully repeated in the preparation of phenylbis(2-cyanoethyl)arsine. diphenyl-2-cyanoethylarsine and methylbis(2-cyanoethyl)arsine The two former compounds have been successfully reduced to the corresponding 3-aminoarsines in good yields by the action of lithium aluminum hydride and identified by various crystalline solid derivatives The aminoarsines

themselves are oils which could not be crystallized. It was expected that the reduction of 2-cyanoarsines by zinc and hydrochloric acid or by gaseous hydrogen under pressure would cause rupture of the arsenic-carbon bonds Consequently, it was very gratifying to obtain these compounds by lithium aluminum hydride reduction.

The following summary is a tabulation of the results obtained for these two new aminoarsines·

	State	m.p.
Phenylbis(3-aminopropyl)arsine	oil	------
Dihydrochloride	solid	210-211ᶜ
Mercuric Chloride Addition Compound	gum	-------
Picric Acid Addition Compound	oil	-------
Platinum Complex	solid	181-183°
Diphenyl-3-aminopropylarsine	oil	--------
Hydrochloride	solid	151-152°
Mercuric Chloride Addition Compound	solid	190-192°
Picric Acid Addition Compound	solid	167-168°
Platinum Complex	solid	152-153°

Benzylbis 2-cyanoethylarsine could not be prepared by a method similar to that employed for the phenyl- and diphenyl- analogs due to the thermal instability of benzylarsine.
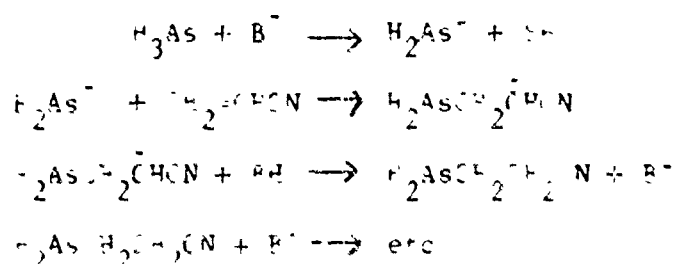
The lithium aluminum hydride reduction of methylbis(2-cyanoethyl)arsine follows a different and unidentified path. Apparently a hydrogenolysis type reaction takes place. Some evidence pointing toward this mode of reaction is the fact that two products were obtained -- one high in carbon and hydrogen and one low in carbon and hydrogen with respect to the desired product. It may be that the aromatic carbon-arsenic bond is sufficiently more stable to resist rupture by lithium aluminum hydride whereas the latter is ruptured.

B.   Possible Existence of Tris 2-cyanoethyl arsine and Tris(3-aminopropyl)arsine

Cookson and Mann were unable to prepare tris(2-cyanoethyl)arsine by the base catalyzed condensation of gaseous arsine with acrylonitrile.

In only one experiment was a small quantity of oil produced by the base catalyzed condensation of gaseous arsine with acrylonitrile   After solidification and recrystallization a very small quantity of solid was obtained having a melting point of 70-79   There was insufficient material for an analysis   This melting range is about what one would expect in the series C_6H_5As $H_2(CH_2CN)_2$ m p 5 - , and $(C_6H_5)_2AsCH_2CH_2CN$ m p 37-39   This work could not be reproduced

If such a condensation is possible a very strong base ill be required to induce a Michael reaction mechanism:

$$H_3As + B^- \longrightarrow H_2As^- + BH$$

$$H_2As^- + CH_2=CHCN \longrightarrow H_2AsCH_2CH_2N$$

$$AsCH_2CHCN + BH \longrightarrow H_2AsCH_2CH_2N + B^-$$

$$H_2As H_2CH_2CN + B^- \longrightarrow etc$$

C.   Possible Existence of Substituted 2-Aminoethyl Arsines

Phenylarsine has been successfully condensed with ethyleneimine in fair yield.   Some evidence has been gathered to indicate that diphenylarsine can likewise be condensed with ethyleneimine   This success forecasts the synthesis of a number of aryl and alkyl 2-aminoethyl arsines and possibly tris(2-aminoethyl)-arsine.

Phenylbis 2-aminoethyl arsine dihydrochloride is much more difficult to isolate than the corresponding 3-aminopropyl compound   Oiling was prevalent and crystallization was extremely slow and tedious   Amine hydrochlorides of organo-metallic compounds are noted as being difficult to obtain as crystalline solids.

Diphenyl-2-aminoethylarsine hydrochloride could not be isolated as a pure compound   It extremely hygroscopic and became oily on brief exposure to air   The only melting point obtained, 110-123 appears consistent with the series

phenylbis(2-aminoethyl)arsine dihydrochloride   184 5-186°

diphenyl-3-aminopropylarsine hydrochloride   151-152°

phenylbis(3-aminopropyl)arsine dihydrochloride   210-211°

Further attempts to 1. .tify this compound by crystalline derivatives likewise

resulted in oils

The following summary is a tabulation of the results obtained for these

two new aminoarsines

	State	m.p.
Phenylbis 2-aminoethyl)arsine		
Dihydrochloride	solid	184.5-186°
Mercuric Chloride Addition Compound	solid	105° (d)
Picric Acid Addition Compound	oil	----------
Oxalic Acid Addition Compound	solid	148.5-150.5°
Diphenyl-2-aminoethylarsine		
hydrochloride	oil	----------
Mercuric Chloride Addition Compound	gum	----------
Picric Acid Addition Compound	oil	----------

D   Reduction of haloarsines with Lithium Aluminum Hydride

Only a few scattered reports have been published regarding the preparation

of arsines by the lithium aluminum hydride reduction of haloarsines. The only

workers to report practical yields were Wiberg and Modritzer. These workers

attempted to produce quinquevalent arsenic hydrides with lithium aluminum

hydride and lithium borohydride As a result they obtained good yields of the

correspondent trivalent arsenic hydrides They conducted their experiments at

low temperatures and with large excesses of hydride. The following is a brief
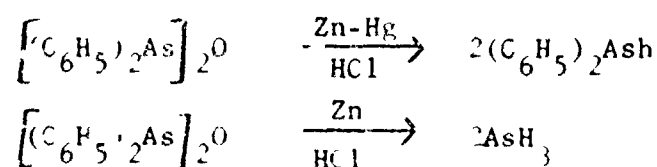
summary of their results·

Starting Materials	Moles Hydride / Moles Haloarsine	Temp	Product	Yield
$C_6H_5AsCl_4$; $LiAlH_4$	5:1	-60°	$C_6H_5AsH_2$	81%
$C_6H_5AsCl_4$; $LiAlH_4$	5:1	-60°	$C_6H_5AsH_2$	75%
$(C_6H_5)_2AsCl_3$; $LiAlH_4$	7:1	-70°	$(C_6H_5)_2AsH$	82%
$(C_6H_5)_2AsCl_3$; $LiAlH_4$	2:1	-95°	$(C_6H_5)_2AsH$	26%

There have been no published reports of the successful preparation of aliphatic arsenic hydrides by the lithium aluminum hydride reduction of haloarsines.

The following is a summary of this work involving the reduction of both aromatic and aliphatic haloarsines with lithium aluminum hydride. The yields of aromatic arsenic hydrides by the amalgamated zinc reduction of the corresponding acid and oxide in hydrochloric acid solution are given for comparison.

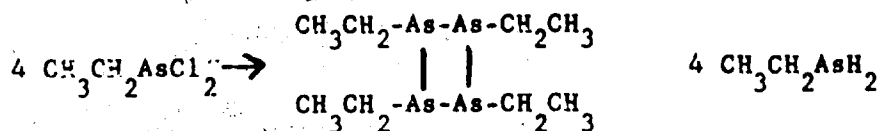| Reactants	Time	Temp.	Yield
$C_6H_5AsCl_6$; $LiAlH_4$	5 hrs	34	31-34%
$C_6H_5AsO_3H_2$; $[]$	24 hrs	25°	75-83%
$(C_6H_5)_2AsCl$; $LiAlH_4$	5 hrs	34°	79%
$\left[(C_6H_5)_2As \right]_2O$ $[]$	48 hrs	25°	71-78%
$CH_3As._2$; $LiAl_4$	20 min	64°	68%
$C_3H_2As\ l_2$; $LiAlH_4$	20 min.	64°	64%

The above results are encouraging for the preparation of arsenic hydrides from arsenic halides. The diphenylarsine yield obtained by the lithium aluminum hydride reduction compares favorably with the yield obtained by the amalgamated zinc reduction and requires a much shorter reaction time. If reaction time is hastened by omission of the mercuric chloride in the zinc reduction, bond cleavage occurs with the result that most of the arsenic is lost as arsine

$$\left[(C_6H_5)_2As \right]_2O \xrightarrow[\text{HCl}]{Zn-Hg} 2(C_6H_5)_2AsH$$

$$\left[(C_6H_5)_2As \right]_2O \xrightarrow[\text{HCl}]{Zn} 2AsH_3$$

The lithium aluminum hydride reduction of diphenylchlorarsine also compares favorably with the results of Wiberg and Mödritzer with lithium borohydride and is much superior to their results using lithium aluminum hydride.

The yield of phenylarsine by the lithium aluminum hydride reduction of phenyldichloroarsine is disappointing. This may be due to incomplete reduction resulting in the formation of arsenobenzene. It is known that the hypophosphorous acid reduction of phenylarsonic acid leads to the formation of arsenobenzene. It is also known that phenylarsine reacts with phenyldichloroarsine under certain conditions. Such a reaction may be minimized by the low reaction temperatures employed by Wiberg and Mödritzer.

The results obtained with aliphatic haloarsines are very encouraging. Incomplete reduction to polymeric arsines may be important. In this respect arsenoethane may be viewed as an intermediate reduction state, e.g.

$$4\ CH_3CH_2AsCl_2 \rightarrow \begin{array}{c} CH_3CH_2-As-As-CH_2CH_3 \\ |\quad\ | \\ CH_3CH_2-As-As-CH_2CH_3 \end{array} \qquad 4\ CH_3CH_2AsH_2$$

A milder reducing agent such as hypophosphorous acid is known to produce such compounds in good yields.

It also appears likely that polymeric arsines may be produced by reaction of the formed arsine with unreacted haloarsine. Removal of the generated arsine as it is formed minimized polymeric arsenic formation by decreasing contact time. If the arsine is not removed rapidly, polymeric arsines can be the major product.